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Gas Sample Storage

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The report gives results of a laboratory evaluation to compare the storage stability of selected gases covering a range of compound categories, in three types of containers: glass bulbs and two different polymeric sample bags. The studies indicate that glass bulbs are the best overall choice, with no significant gas losses. Reactive and highly polar gases were preferentially lost from samples stored in the polymeric bags. Some contaminants were detected in the samples taken from the polymeric sample bags, presumably the result of outgassing from the materials used to construct the bags.

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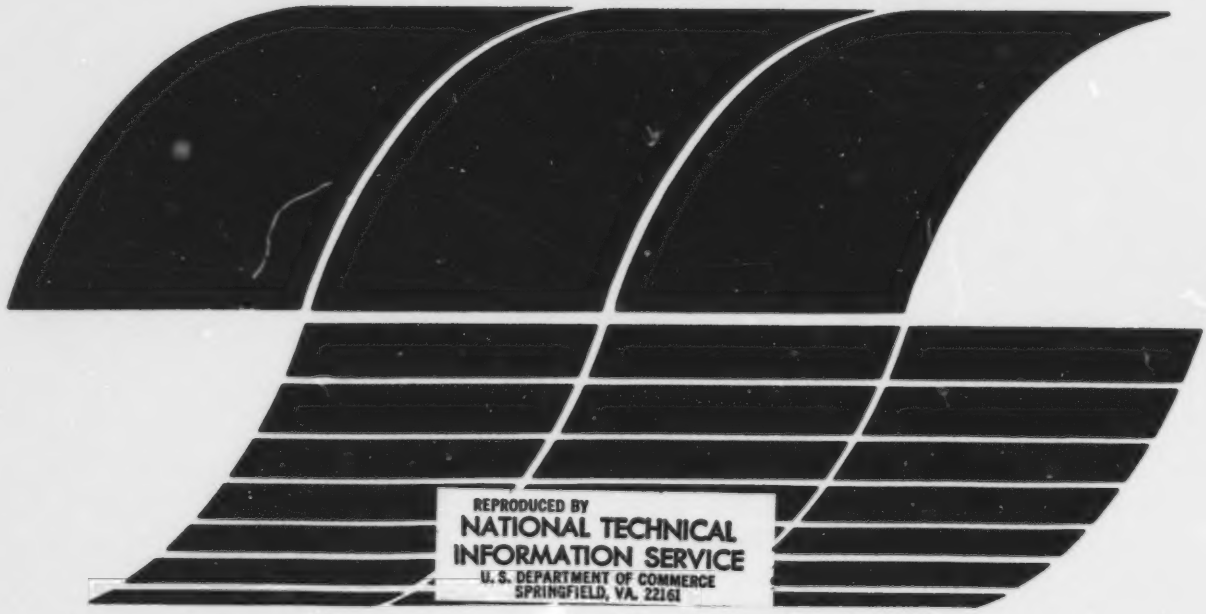

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April 1979

Gas Sample Storage

by

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ABSTRACT

A laboratory evaluation has been conducted to compare the storage stability of selected gases covering a range of compound categories, in three types of containers including glass bulbs and two different polymeric sample bags.

The studies indicated that glass bulbs are the best overall choice, with no significant losses of gases. Reactive and highly polar gases were preferentially lost from samples stored in the polymeric bags. Some contaminants were detected in the samples taken from the polymeric sample bags, presumably the result of outgassing from the materials used to construct the bags.

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I. SUMMARY

The suitability of several types of containers for the long-term storage of gas samples was compared in a laboratory study. The performances of glass bulbs and polymeric bags from two vendors were evaluated. A test gas mixture consisting of ethane, propylene, methyl chloride, methanol, ethylene oxide and benzene was prepared in order that the behavior of compounds of differing molecular weights and polarity could be studied. The test gas mixture was introduced into each of the three containers and the concentrations of the individual gaseous compounds were measured as a function of storage time, using gas chromatography.

The studies indicated that glass bulbs are the best overall choice, with no significant losses of the gases. Reactive and highly polar gases were preferentially lost in the polymeric sample bags. Relatively simple gases were stable in these sample bags. Contaminants were detected in the samples taken from the polymeric bags, presumably the result of outgassing from the construction materials of the bags. These contaminants were found at very low ppb levels, but they could nevertheless interfere with ultratrace analyses of collected gas samples. Therefore, the polymeric bags are recommended for the storage of relatively simple gases at high concentration levels, i.e. ppm or greater. The calibrated Instrument's 5-layered bags were superior to the Dupont Tedlar bags, with fewer interferences and less sample loss.

II. INTRODUCTION

Environmental assessment sampling and analysis studies frequently necessitate the detection, identification and quantification of very small concentrations of gaseous organic compounds. Gases are defined, in this study, to be those species with an approximate boiling point range similar to those of the C1-C7 hydrocarbons, i.e., -160°C to 100°C.

The analysis of gaseous organic components requires that suitable sampling methods be used. Representative samples must be collected, and their integrity preserved between the sampling and analysis interval. Several factors contribute to sample loss and contamination when collecting, storing and analyzing gas samples. Major problems that have been reported in the literature include sample container permeability, reactivity, adsorption, condensation, "memory effect" from reusing containers, and contaminants in the container.

The objective of this study was to demonstrate what kinds of container materials are most suitable for storing organic compounds of environmental interest, i.e., containers demonstrating the least amount of container/compound interactions.

Stability was demonstrated by a laboratory evaluation of gas sample storage as a function of time and container composition, keeping the other variables as constant as possible. Gas storage stability in two types of polymeric bags and glass bulbs were compared. The containers chosen for the study are described in Section IV. The Dupont Tedlar and Calibrated Instruments 5-layered bags were chosen as being constructed of materials representative of the types of polymeric materials currently (1978) in use, and showing relatively high stablity for gas sample storage. Ace Thred glass containers, which are frequently used for collecting gas samples, were also evaluated.

Studies have been completed for six compounds--ethane, propylene, methyl chloride, methanol, ethylene oxide and benzene--in the three containers. This mixture was chosen to cover a range of compound categories. The preparation of the mixture is described in Section IV.

III. BACKGROUND

Literature Review

A number of papers have been published discussing methods for sampling and analysis of gases. These have been reviewed to identify important factors contributing to sample loss and contamination when collecting, storing and analyzing gas samples. The variables identified were container composition, size and preconditioning, storage time, temperature, relative humidity of sample air, lighting conditions, sample composition and concentration, and methods of sample collection.

Baker[1] compared storage of various gases in steel cylinders, plastic bags and glass flasks. Compression storage in steel cylinders was adequate for hydrocarbons but resulted in high losses of sulfur dioxide and nitrogen dioxide. Baker evaluated Mylar (polyester film), aluminized Mylar Saran wrap type 12 (polyvinyidene chloride film), Saran wrap drum liner, Scotchpak 20A5 (polyester film) and aluminized Scotchpak 20A5 as storage containers for gases at atmospheric pressure. Permeability of gases and vapors through polymeric films is a function of temperature, polymeric sidechains, plasticizers and H_2O.[2]

Moisture was a major factor in the polymeric bags; mineral oxides disappeared at high relative humidity. Hydrocarbon loss was controlled by diffusional changes alone and showed only minor changes. Acetone and benzene showed little change, and 2-pentene showed minor losses.

The two-layer bags (aluminized Scotchpak and Mylar) reduced the moisture problem. A sulfur dioxide, nitrogen dioxide, and 2-pentene mixture stored in stainless steel containers at atmospheric pressure showed no significant loss. Comparable storage in glass flasks showed high loss of sulfur and nitrogen dioxides.

Clemens[3] further found Mylar to show no systematic changes in paraffinic hydrocarbon concentration over a period of ten days. A major portion of the aromatic hydrocarbons were lost after a few days.

Some of the aromatic hydrocarbons later reappeared in the vapor space of the container.

Conner[4] used Mylar and Teflon containers to study the storage of NO_2, SO_2, O_3 and hydrocarbons. Teflon bags were found to be inferior to Mylar for containing SO_2, NO_2, and O_3, and offered no noticeable advantage for storing hydrocarbons. Preconditioning Mylar bags with SO_2 and O_3 improved their storage, but Mylar could not be conditioned to NO_2 and hydrocarbons.

Glass containers are known for major losses of sulfur compounds, apparently due primarily to surface adsorption. Wright[5] investigated Teflon and Tedlar bags for sulfur compound storage. Initial losses in Tedlar and Teflon bags were found to be similar. However, after 160 hours the Tedlar bags retained 75% of the sulfur compounds, while Teflon retained only 25%.

Schuetzle[6] used hydrocarbon and odor measurements to evaluate sampling procedures. Polyethylene, Saran and Mylar bags were found to be unsuitable for storing organic emissions, whereas standards and samples stored in Tedlar bags have shown less than 10% average hydrocarbon loss over a period of several days. It was found that most errors affecting odor and hydrocarbon concentration values of gas samples in Tedlar bags occurred when collecting warm (>30°C), highly concentrated, or very polar organic gases. Errors were reduced by 1). minimizing adsorptive effects by increasing bag size and conditioning in evacuated containers, 2). pressurizing with a non-odorous gas, and prediluting the sample, 3). dynamically diluting warm (>30°C) stack gases and 4). removing container contaminants by flushing with dry air at 80°C for approximately 2 hours.

Levine[7] compared vinyl chloride monomer (VCM) gas storage in Teflon and aluminized Scotchpak 3-layered bags (Calibrated Instruments). The Teflon bag showed a loss of VCM in the range of 20% per day. There

was no detectable loss of VCM in the aluminized Scotchpak, 3-layered bag for a period of one week.

Polasek[8] evaluated a bag sequential sampling technique for ambient air analysis. To determine the influence of bag materials on samples, calibration gas containing carbon monoxide, non-methane hydrocarbons and methane was placed in the bags and then analyzed at 0, 24, 48 and 100 hours. The results indicated that polyvinyl chloride bags were satisfactory for sample storage (up to about 15 hours), whereas Tedlar bags were, in general, unsatisfactory for sample storage. Polasek stated that the 5-layered bags were excellent for long-term storage of carbon monoxide, but completely unacceptable for non-methane hydrocarbons. Aluminized polyester bags, consisting of a layer of polyester on both sides of an aluminum layer, were excellent for long-term storage of both carbon monoxide and non-methane hydrocarbons.

VanHaam[9] investigated possible interferences from low molecular weight additives in polyvinyl fluoride (PVF: "Tedlar") used for the construction of smog chambers. Organic compounds released from Tedlar interfered with (total) hydrocarbon concentration, NO_X response and hydrocarbon/NO_X ratio measurements. It was also observed that ozone and peroxyacetyl nitrate were formed in the bags. The interference decreased with increasing surface to volume ratio.

Dimitriades[10] used Tedlar (2 mil thick) bags to investigate the development of procedures for routine analysis of automotive fuels and the hydrocarbon of exhaust emissions. Tedlar was found to lead to losses of individual hydrocarbons on or through bag walls, of 5 to 6%. Acetone was observed to be lost by permeation through the Tedlar walls. Acetaldehyde and butyraldehyde levels did not change significantly, whereas benzaldehyde disappeared completely within 0.5 hr. Epoxides of ethylene and 1-butene were somewhat unstable. It was also observed that adsorption and accumulation of adsorbable material occured on the gas chromatography (GC) sample loop, used for sample introduction. Errors in analyzing gas mixtures were reduced by:

1) increasing the container size, to minimize water condensation and slow down reaction among sample components;

2) keeping the Tedlar bags in a dark cloth bag, to reduce light induced reactions;

3) keeping sampling lines and proportional sampling device at 80°C, to prevent water condensation and subsequent loss of water soluble components; and

4) heating the loop to 110°C, to minimize sample adsorption and build-up in the GC sampling loop.

Vinyl chloride monomer (VCM) gas storage in 5-layered bags was studied by the Independent Research Division for Gases of the Linde Corporation, for Calibrated Instruments[11]. Minor losses of analyte were found after periods of 8 days and 8 weeks. Other tests performed were: 1) bursting strength, 2) aging, 3) change of gas composition, 4) total gas losses at changing temperatures, 5) analytical measurements of dilution losses of individual components, and 6) determination of losses of gas components through permeation. The overall performance of the 5-layered bag was found to be quite good.

Based upon the information available in 1978, the Tedlar bags, 5-layered bags and glass bulbs appeared to be suitable containers to consider using for gas sampling. The literature review indicated that contamination, absorption and permeation problems in the 5-layered bags were somewhat less than in the Tedlar bags. The polymeric bags appeared to offer significant advantages compared to glass bulbs in terms of handling in the field and shipping gas samples to the laboratory for analysis.

IV. EXPERIMENTAL

A. Approach

This study of gas sampling and storage looked at sample storage stability as a function of time and container composition. Light was excluded from all of the containers, as much as possible, to eliminate potential light reactions. The approach taken involved adding a known concentration of a test gas mixture into a container and measuring the gas concentration levels as a function of time. Replicate sample data were used to calculate the mean measured value, standard deviation and coefficient of variation, at predetermined times.

Experiments were conducted with a test gas mixture representative of several categories of compounds. The components of the mixture are described in Table 1.

The specific components of the mixture were chosen to represent a range of chemical reactivities, and to be of environmental interest. Where possible, compounds with low toxicity to the analyst were chosen from the compound categories. The three types of containers studied, described in Table 2, were the 5-layered bag, Tedlar bag and Ace-Thred glass collecting bulbs. These containers are generally representative of the various container compositions currently being used for storing samples.

The literature review (Section III) indicated that surface adsorption may be a problem with polar organic gases. Suggestions were made that increasing the container size and preconditioning may to some degree eliminate the problem. Some experiments were run to evaluate whether or not preconditioning the polymeric bags with methanol would decrease methanol concentration losses due to absorption into the walls of the bags.

TABLE 1

Test Gas Mixture

Compound Category	Compounds	Composition	MATE (12) Air[a]	MATE (12) Water[a]	MW[b]	BP °C	Retention Time on Porapak Q[c] Minutes
Aliphatic Hydrocarbon	Ethane	C_2H_6	6.1E6		30	-89	35
Aliphatic Hydrocarbon	Propylene	C_3H_6	8.6E6	1.3E8	42	-47	18.5
Alkyl Halide	Methyl Chloride	CH_3Cl	2.1E5	3.2E6	50	-24	22.5
Alcohols	Methanol	CH_3OH	2.6E5	3.9E6	32	64	27
Epoxides	Ethylene Oxide	C_2H_4O			44	11	50
Benzenes	Benzene	C_6H_6	3.0E3	4.5E4	78	80	30.5[d]

(a) Health effects basis ($\mu g/m^3$ air and $\mu g/L$, water).
(b) Monoisotopic, lightest isotope of each atom.
(c) 2m x 2mm I.D. Porapak Q (waters), 100/120 mesh, glass column, 65°C isothermal, He= 20 mLs min^{-1}.
(d) 2m x 2mm I.D. Porapak Q (waters), 100/120 mesh, glass column, 130°C isothermal, He= 20 mLs min^{-1}.

TABLE 2

Gas Sampling Containers

Container	Vendor	Material Composition	Volume	Surface Area	Comments
5-Layered Bags	Calibrated Instruments	From Innermost Layer High Density Poly Ethylene - 75 μm Polyamide - 40 μm Aluminum Foil - 12 μm Polyvinylidene Chloride - 4 μm Polyethylene Terephthalate - 12 μm	2L	1100 cm^2	Fitted with self-sealing septum, on/off valve hose/bib combination, shape snout-type
Tedlar Bags	Dupont	Polyvinyl Fluoride - 51 μm	4L	1800 cm^2	fitted with on/off valve hose/bib combination.
Glass Collecting Bulbs	Ace-Thred	Glass	2L	950 cm^2	fitted with septum sampling port and Ace-Thred valve.

B. Sample Preparation and Analysis

1. Test Gas Mixture

The sample mixture purchased from Matheson Gas Products, consisted of ethane, propylene, methyl chloride, benzene and methyl alcohol in nitrogen at 10,000 ppm (v/v) each. Ethylene oxide, also purchased from Matheson Gas Products, was available in a separate gas cylinder and was added separately. The components in the mixture were chosen to cover a range of compound categories and boiling points, and were of generally low toxicity. The test gas mixture was added into the three types of sample containers to a concentration level of 100 ppm. All the components in the mixture, except benzene, could be analyzed in a single gas chromatography (GC) experiment, as described in Section B.7. Benzene was analyzed separately.

It was originally intended to use air as the diluting gas in this study. Blanks were run on the 5-layered bag samples containing 2 liters of air (Matheson air, zero gas). The sample mixture was spiked into the 5-layered bags containing 2 liters of air.

During the determination of gas chromatographic conditions, an unacceptable baseline and several extraneous gas chromatographic peaks, interfering with the sample mixture peaks, were observed. These interfering peaks gradually increased with repetitive sample and blank injections. Subsequent experiments indicated that multiple injections of air on the Porapak Q column appeared to cause the interfering peaks. A Durapak GC column was tried as a substitute for the Porapak Q; however, methanol was not eluted from the column.

When nitrogen gas (tapped from a liquid nitrogen cylinder) was substituted for the air, no interfering peaks were observed on

the Porapak Q column. Nitrogen gas, therefore, was chosen as the diluting gas for the study. Nitrogen gas produced an acceptable baseline on the gas chromatogram and no interfering GC peaks.

Losses in analyte concentration values are limited to container/compound interactions, when nitrogen is used as the diluting gas. Analyte and container reactions with air could introduce additional problems.

2. 5-Layered Bags

Data were obtained by analyzing five replicate samples of two sets of 5-layered bags (sample series A and A') at intervals up to 14 days. The 5-layered bags were purged with nitrogen at least twice. Two liters of nitrogen were then metered into the containers. The gas sample mixture was added with a gas tight syringe to give an approximate concentration of 100 ppm. Five sample mixtures were each analyzed immediately after preparation (at 0 hours) and stored in a dark, dry cabinet. The 5-layered bag samples were subsequently analyzed at predetermined times. Sample introduction was made via a gas-sampling loop, directly from the bag.

Because benzene could not be analyzed under the GC conditions used for the other five sample components (IV.B.7), the benzene concentration was not determined at each of the predetermined storage time intervals. Benzene stability in the sample mixture was evaluated based on the concentration measured after 53 days of sample storage.

3. Tedlar Bags

Data were obtained by analyzing five replicate samples in the Tedlar bags (sample series B), at intervals up to 14 days. Complete sample loss was observed with the 2-liter Tedlar bags

originally obtained, and it was found that they leaked. Four-liter Tedlar bags obtained from a different supplier were satisfactory. The bags were wrapped with aluminum foil, to exclude light as much as possible, and purged with nitrogen at least twice. Two liters of nitrogen were then metered into the containers. The gas sample mixture was added to the Tedlar bags to an approximate concentration of 100 ppm, using a gas-tight syringe. Five sample mixture replicates were each analyzed immediately (at 0 hour) and then stored in a dark, dry cabinet. The Tedlar bag samples were subsequently analyzed at predetermined times. Sample introduction into the gas chromatography column was made via a gas sampling loop.

Benzene data were obtained after the basic time study was completed, i.e., after 51 days of storage (please refer to Section IV-B-7).

4. Glass Bulbs

Data were obtained by analyzing four replicates of the Ace-Thred glass bulb samples at intervals up to 14 days.

The glass bulbs were wrapped with aluminum foil to exclude light, and purged with a stream of nitrogen. Two liters of nitrogen were metered into the containers. The gas sample mixture was added to an approximate concentration of 100 ppm, using a gas-tight syringe. Sample withdrawal from the glass bulb was made with a gas-tight syringe, and sample introduction onto the gas chromatograph column was done via a gas-sampling loop. Four sample mixture replicates were each analyzed immediately after spiking (at 0 hour) and stored in a dark, dry cabinet. The glass bulb samples were subsequently analyzed at predetermined times.

Benzene data were obtained after the basic time study was completed, i.e., after 15 days of storage (please refer to Section IV-B- 7).

5. Nitrogen Blanks in the 5-Layered and Tedlar Bags

The 5-layered and aluminum foil covered Tedlar bags were purged with nitrogen at least twice. Two liters of nitrogen were then metered into the containers. Samples were introduced onto the gas chromatograph column via a gas sampling loop. The detector sensitivity was increased ten fold, compared to that used for samples.

6. Analysis of Methanol in 5-Layered and Tedlar Bags Preconditioned with Methanol

The 5-layered and aluminum foil covered Tedlar bags were filled with nitrogen. Methanol was subsequently added to the Tedlar and 5-layered bags and equilibrated. The containers were then emptied. This procedure was followed three times, in order to precondition the inner walls of the two types of containers with methanol. After preconditioning, two liters of nitrogen were metered into duplicate Tedlar and 5-layered bags. Methanol was added to the containers to a concentration of 100 ppm. Data were obtained at intervals up to seven days.

7. Analysis

Gas Chromatographic Conditions

Sample introduction on the Varian 2700 GC was made via a 1.0 mL gas sampling loop and valve. Gas chromatographic (GC) conditions were investigated using a 2m x 2mm I.D., Porapack Q (Waters), 100/200 mesh, glass column. The

optimal conditions for chromatography of the gas sample mixture were determined to be:

Column Temperature:	65°C, isothermal
Helium flow:	20 mLs/min
Injection temperature:	200°C
Detector temperature:	240°C

Under these conditions, the retention times for each of the model compounds were: ethane - 3.5 minutes, propylene - 18.5 minutes, methyl chloride - 22.5 minutes, methanol - 27 minutes, and ethylene oxide - 50 minutes. A gas chromatogram is presented in Figure 1. Benzene, however, had an unacceptably long retention time under these conditions. Temperature programming was investigated, but this resulted in unacceptable baseline drift. Benzene was quantified in separate experiments at an isothermal temperature of 130°C. At this temperature, the retention time for benzene was 30.5 minutes.

Fresh calibration standards were prepared daily at concentration levels of 200 ppm (v/v), 100 ppm (v/v) and 50 ppm (v/v). Standard curves were drawn for each of the model compounds, and used to calculate the concentration values.

It was observed that the retention times of the sample GC peaks gradually increased with repetitive sample injections. The column temperature therefore had to be increased to 85°C isothermal, so that the analysis time would remain reasonable. i.e., less than 1 hour per sample. There seemed to be some serious stability problems associated with the use of Porapak Q.

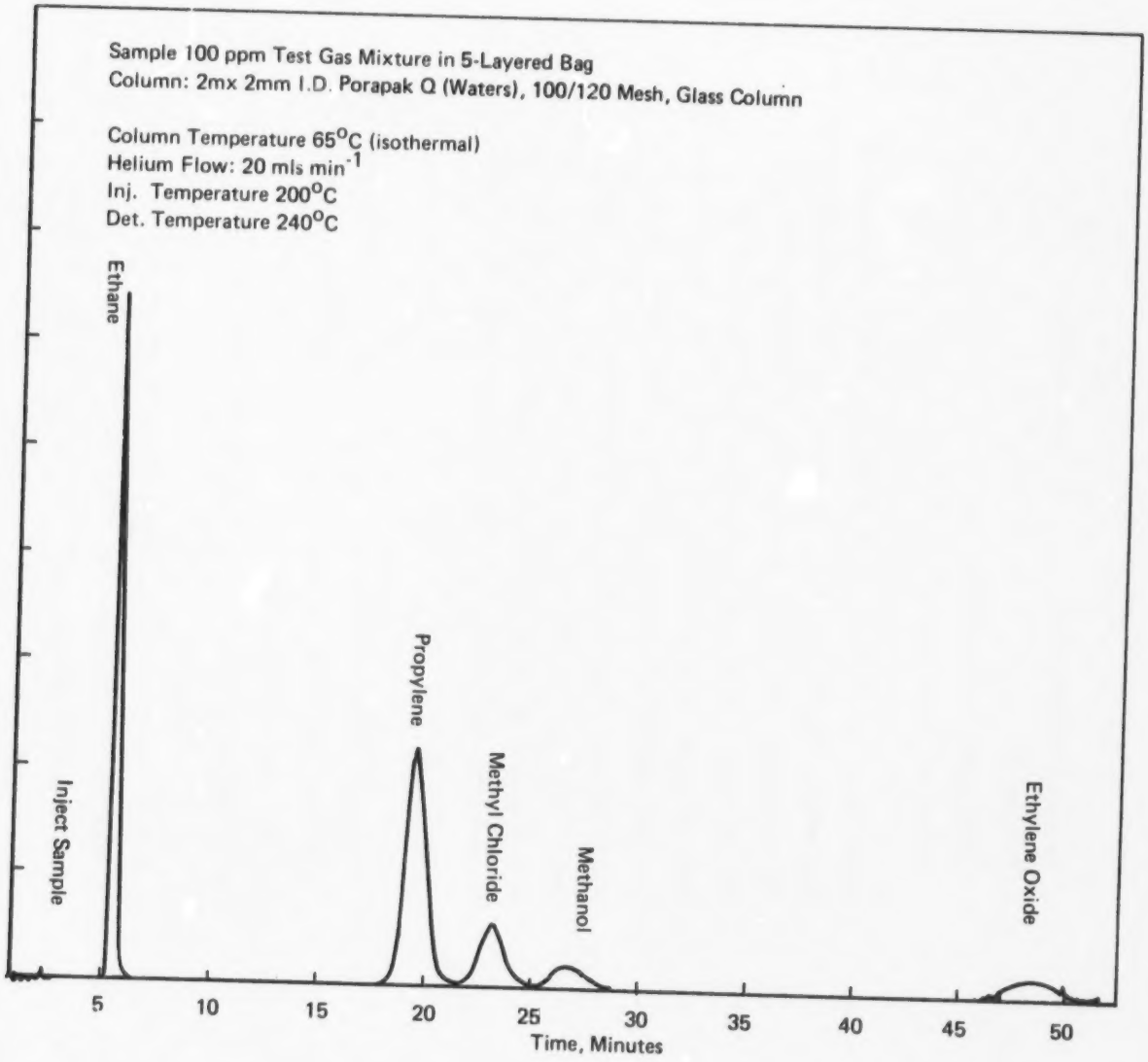

FIGURE 1 GAS CHROMATOGRAM OF GAS MIXTURE

V. RESULTS AND DISCUSSION

A. 5-Layered Bags

Data were obtained for two sets of bags spiked with the test gas mixture, at intervals up to 14 days of storage. The data are presented in Tables 3, 4, and 5. The mean, $(\bar{X})$, standard deviation (σ), and coefficient of variation (CV) were calculated for each set of five replicates.

Five of the six model compounds are apparently stable for up to 14 days of storage. Ethane, propylene, methyl chloride, ethylene oxide and benzene show no apparent trend towards loss or gain.

The ethylene oxide data are presented in Table 5. The replicate data at each time period have high coefficients of variation. The syringe used for adding the ethylene oxide may have been plugged, causing this high variability. Therefore, the ethylene oxide data are presented for each container. The coefficient of variation for ethylene oxide concentration in any given container is low, and there do not appear to be any significant losses or gains. Ethylene oxide appears to be stable in the Calibrated Instrument 5-layered bags.

The methanol data in both sets of bags have high coefficients of variation, and apparent losses over 14 days. The overall methanol concentration loss in the replicate bags is 50%. The loss appears to occur within the first 24 hours. The first set of 5-layered bags (A) has an 86% loss at 3 days. This loss is not replicated and may be due to experimental error. The methanol concentration losses may be due to permeation through or absorption on the walls of the 5-layered bags.

Benzene was quantified in duplicate 5-layered bags, after 53 days of storage. The calculated mean concentration at 53 days

TABLE 3

Gas Sampling Study Analytical Data

Sample Container: Calibrated Instrument's 5-Layered Bags (A)

COMPOUND CONCENTRATION, ppm* (v/v)

Sample / Time	Ethane	Propylene	Methyl Chloride	Methanol
1A /0 hrs	110	109	100	110
2A	115	115	115	110
3A	104	130	115	93
4A	109	110	90	83
5A	104	105	95	93
	$\bar{X}$ = 109	$\bar{X}$ = 114	$\bar{X}$ = 103	$\bar{X}$ = 98
	σ = 5	σ = 9	σ = 12	σ = 12
	CV = 4%	CV = 8.5%	CV = 11.2%	CV = 12.1%
1A/ 1 day	104	106	100	50
2A/	105	110	115	39
3A/	105	105	100	50
4A/	117	110	96	65
5A/	103	108	100	57
	$\bar{X}$ = 107	$\bar{X}$ = 108	$\bar{X}$ = 102	$\bar{X}$ = 52
	σ = 6	σ = 2	σ = 7	σ = 10
	CV = 4 %	CV = 2.2%	CV 7.2%	CV = 18.4%
1A/ 3 days	104	113	103	10
2A/	108	108	103	10
3A/	115	104	103	21
4A/	109	110	95	10
5A/	104	106	103	21
	$\bar{X}$ = 107	$\bar{X}$ = 108	$\bar{X}$ = 101	$\bar{X}$ = 14
	σ = 5	σ = 3	σ = 3	σ = 6
	CV = 4.5%	CV = 3.2%	CV = 3.5%	CV = 41.8%

*ppm - Calculated from a standard curve. (Concentration vs. Peak Area)
Mean = $\bar{X}$
Standard Deviation = σ
Coefficient of Variation = $\sigma/\bar{X}$ = CV

TABLE 3 (Cont'd)

Gas Sampling Study Analytical Data

Sample Container: Calibrated Instrument's 5-Layered Bags (A)

COMPOUND CONCENTRATION, ppm* (v/v)

Sample / Time	Ethane	Propylene	Methyl Chloride	Methanol
1A/14 Days	118	111	95	36
2A/	118	111	107	36
3A/	111	104	116	40
4A/	111	107	98	32
5A/	111	107	103	28
	$\bar{X}$ = 114	$\bar{X}$ = 108	$\bar{X}$ = 109	$\bar{X}$ = 34
	σ = 4	σ = 3	σ = 8	σ = 5
	CV = 3.4%	CV = 2.7%	CV = 7.4%	CV = 13.2%

*ppm = Calculated from a standard curve. (Concentration vs. Peak Area)
Mean = $\bar{X}$
Standard Deviation = σ
Coefficient of Variation = $\sigma/\bar{X}$ = CV

TABLE 4

Gas Sampling and Storage Study Analytical Data

(Sampling Container: Repeat Calibrated Instrument's 5-Layered Bag (A')

COMPOUND CONCENTRATION, ppm* (v/v)

Sample / Time	Ethane	Propylene	Methyl Chloride	Methanol
1A'/0 hr	105	109	92	84
2A'	107	115	98	93
3A'	117	115	115	93
4A'	117	111	106	73
5A'	122	112	106	111
	$\bar{X}$ = 114	$\bar{X}$ = 112	$\bar{X}$ = 103	$\bar{X}$ = 91
	σ = 7	σ = 3	σ = 9	σ = 14
	CV = 6.4%	CV = 2.3%	CV = 8.4%	CV = 15%
1A'/ 1 day	105	100	103	62
2A'/	108	102	95	50
3A'/	113	105	90	32
4A'/	105	107	95	40
5A'/	110	102	100	10
	$\bar{X}$ = 108	$\bar{X}$ = 103	$\bar{X}$ = 97	$\bar{X}$ = 39
	σ = 3	σ = 3	σ = 5	σ = 20
	CV = 3.2%	CV = 2.7%	CV = 5.2%	= 39%

* ppm = Calculated from a standard curve. (Concentration vs. Peak Area)
Mean = $\bar{X}$
Standard Deviation = σ
Coefficient of Variation = $\sigma/\bar{X}$ = CV

TABLE 4 (Cont'd)

Gas Sampling and Storage Study Analytical Data

Sampling Container: Repeat Calibrated Instrument's 5-Layered Bag (A')

COMPOUND CONCENTRATION, ppm* (v/v)

Sample / Time	Ethane	Propylene	Methyl Chloride	Methanol
1A'/8 days	97	102	95	68
2A'	93	96	83	20
3A'	49	1[illegible]	95	29
4A'	101	1[illegible]	100	32
5A'	99	[illegible]	83	50
	$\bar{X}$ = 98	$\bar{X}$ = 99	$\bar{X}$ = 91	$\bar{X}$ = 40
	σ = 3	σ = 4	σ = 8	σ = 19
	CV = 3.1%	CV = 3.6%	CV = 8.5%	CV = 48%
1A'/14 days	95	97	92	57
2A'	95	98	88	42
3A'	95	97	111	45
4A'	95	99	92	47
5A'	102	97	92	62
	$\bar{X}$ = 96	$\bar{X}$ = 98	$\bar{X}$ = 95	$\bar{X}$ = 51
	σ = 3	σ = 1	σ = 9	σ = 9
	CV = 3.2%	CV = .9%	CV = 9.5%	CV = 16.8%

*ppm = Calculated from a standard curve. (Concentration vs. Peak Area)
Mean = $\bar{X}$
Standard Deviation = σ
Coefficient of Variation = $\sigma/\bar{X}$ = CV

TABLE 5

Gas Sampling Study Analytical Data

Sample Container: Calibrated Instruments 5-layered Bags (A and A')

Ethylene Oxide Concentration, ppm (v/v)

Sample/Time	1A	2A	3A	4A	5A
0 hour	75	58	27	27	27
1 day	46	40	25		
1.5 days					36
3 days	61	44	27	27	32
7 days					46
14 days	70	51	25	23	32
$\bar{X}$ =	63	48	26	26	35
σ =	13	8	1	2	7
CV =	20.2%	16.4%	4.4%	8.9%	20.5%

Sample/Time	1A'	2A'	3A'	4A'	5A'
0 hour					50
1 day	120	99	96	84	59
8 days	110	98	91	79	42
14 days	121	125	106	91	52
$\bar{X}$ =	117	107	98	85	51
σ =	6	15	8	6	7
CV =	5.1%	14.2%	7.8%	7.1%	13.8%

was 79 ppm. This does not appear to be a significant loss as compared to an original 100 ppm spike. Benzene appears to be stable in the calibrated instrument's 5-layered bags.

B. Tedlar Bags

Data were obtained for the Tedlar bag samples spiked with the test gas mixture, at intervals up to 14 days of storage. The data are presented in Table 6. The mean ($\bar{X}$), standard deviation (σ) and coefficient of variation (CV) were calculated for each set of 5 replicates.

Four of the six model compounds are apparently stable up to 14 days of storage. Ethane, propylene, methyl chloride and benzene show no apparent trend towards loss or gain within the calculated CV of the replicate values.

Benzene was quantified in 3 replicate Tedlar bags, after 51 days of storage. The calculated mean concentration at 51 days was 126 ppm. This does not appear to be significantly higher than the original 100 ppm spike concentration, within the precision of the measurement. Benzene, therefore, appears to be stable in the Dupont Tedlar bags.

The methanol data show apparent losses at 1 day, 3 days, 7 days and 14 days. The Tedlar bag samples show a mean methanol concentration of 72 ppm at 0 hour, 51 ppm at 1 day, 59 ppm at 3 days, 38 ppm at 7 days and 0 ppm at 14 days. The percentage loss with time is 29% at 1 day, 28% at 3 days, 48% at 7 days and 100% at 14 days. The coefficients of variation for the replicate Tedlar bag samples at any given time are smaller than those calculated for the 5-layered bags. The methanol concentration decreases may be due to permeation through, or adsorption on, the walls of the Tedlar bags.

TABLE 6

Gas Sampling Study Analytical Data

Sample Container: Tedlar Bags (B)

COMPOUND CONCENTRATION, ppm* (v/v)

Sample / Time	Ethane	Propylene	Methyl Chloride	Methanol	Ethylene Oxide
1B/0 hrs	93	96	100	65	109
2B	93	96	104	65	98
3B	104	96	95	74	80
4B	101	95	95	89	46
5B	95	101	87	65	84
	$\bar{X}$ = 97	$\bar{X}$ = 97	$\bar{X}$ = 96	$\bar{X}$ = 72	$\bar{X}$ = 61
	σ = 5	σ = 2	σ = 6	σ = 11	σ = 29
	CV = 5.2%	CV = 2.4%	CV = 6.6%	CV = 14.6%	CV = 46.9%
1B/1 day	87	101	87	50	46
2B	89	101	87	50	67
3B	95	96	95	50	59
4B	99	99	95	59	46
5B	99	97	91	47	59
	$\bar{X}$ = 94	$\bar{X}$ = 99	$\bar{X}$ = 91	$\bar{X}$ = 51	$\bar{X}$ = 55
	σ = 6	σ = 2	σ = 4	σ = 5	σ = 9
	CV = 5.9%	CV = 2.3%	CV = 4.4%	CV = 8.8%	CV = 16.5%
1B/3 days	107	97	101	60	35
2B	96	104	108	57	48
3B	105	102	105	60	46
4B	107	102	105	57	27
5B	105	99	97	60	50
	$\bar{X}$ = 104	$\bar{X}$ = 101	$\bar{X}$ = 103	$\bar{X}$ = 59	$\bar{X}$ = 41
	σ = 5	σ = 3	σ = 4	σ = 4	σ = 10
	CV = 4.4%	CV = 2.7%	CV = 4.1%	CV = 2.8%	CV = 23.9%

*ppm = Calculated from a standard curve. (Concentration vs. Peak Area)

Mean = $\bar{X}$

Standard Deviation = σ

Coefficient of Variation = $\sigma/\bar{X}$ = CV

TABLE 6 (cont'd)

Gas Sampling Study Analytical Data

Sample Container: Tedlar Bags (B)

COMPOUND CONCENTRATION, ppm* (v/v)

Sample / Time	Ethane	Propylene	Methyl Chloride	Methanol	Ethylene Oxide
1B/7 days	105	101	103	38	39
2B	103	101	99	40	56
3B	103	100	99	37	52
4B	103	99	107	42	96
5B	105	97	110	35	65
	$\bar{X}$ = 104	$\bar{X}$ = 100	$\bar{X}$ = 104	$\bar{X}$ = 38	$\bar{X}$ = 62
	σ = 1	σ = 2	σ = 5	σ = 3	σ = 21
	CV = 1.1%	CV = 2%	CV = 4.7%	CV = 7%	CV = 34.7%
1B/14 days	96	118	94	0	36
2B	98	118	98	0	48
3B	123	121	94	0	48
4B	123	118	94	0	36
5B	123	113	86	0	51
	$\bar{X}$ = 112	$\bar{X}$ = 118	$\bar{X}$ = 93	$\bar{X}$ = 0	$\bar{X}$ = 44
	σ = 14	σ = 3	σ = 4	σ = 0	σ = 7
	CV = 12.6%	CV = 2.4%	CV = 4.7%	CV = 0	CV = 16.5%

*ppm = Calculated from standard curve. (Concentration vs. Peak Area)
Mean = $\bar{X}$
Standard Deviation = σ
Coefficient of Variation = $\sigma/\bar{X}$ = CV

The ethylene oxide data in the Tedlar bags show high coefficients of variation and indicate a slight loss in the concentration level. The data indicate that the high coefficients of variation for the Tedlar bags, unlike those for the 5-layered bags, cannot simply be attributed to a high coefficient of variation in the initial concentrations. The Tedlar bags have a mean ethylene oxide concentration of 51 ppm at 0 hour, 55 ppm at 1 day, 41 ppm at 3 days, 62 ppm at 7 days and 44 ppm at 14 days. It should be noted however, that the percentage loss with time is not significantly larger than the coefficient of variation for this analysis.

C. Glass Bulbs

Data were obtained for the glass bulb samples spiked with test gas mixture up to 14 days of storage and are presented in Table 7. The mean, standard deviation and coefficient of variation have been calculated for each set of 4 replicates.

All six model compounds are apparently stable for up to 14 days of storage.

Ethane, ethylene oxide, propylene, and methyl chloride show no changes in concentration that are significant when compared to the coefficient of variation calculated for replicate samples.

Methanol shows no significant trend towards loss or gain up to 14 days, when compared to the calculated coefficients of variation for the measurements. There is an apparent increase in the methanol concentration, 39% in fourteen days, and the coefficients of variation are large, 14.5% to 39.2%. These observations may be due to the effects of the gas sample mixture equilibrating and may reflect mixing difficulties in the glass bulbs.

TABLE 7

Gas Sampling Study Analytical Data

Sample Container: Ace Thred Glass Bulbs (C)

COMPOUND CONCENTRATION, ppm* (v/v)

Sample / Time	Ethane	Propylene	Methyl Cloride	Methanol	Ethylene Oxide
1C/0 hr	96	89	83	76	106
2C	101	99	92	67	95
3C	108	108	108	84	98
4C	105	113	120	60	103
	$\bar{X}$ = 101	$\bar{X}$ = 102	$\bar{X}$ = 101	$\bar{X}$ = 72	$\bar{X}$ = 99
	σ = 6	σ = 11	σ = 17	σ = 10	σ = 3
	CV = 6.1%	CV = 10.3%	CV = 16.3%	CV = 14.5%	CV = 3.4%
1C/1 day	100	96	103	48	107
2C	95	96	98	76	93
3C	111	116	130	56	103
4C	111	121	135	100	102
	$\bar{X}$ = 104	$\bar{X}$ = 107	$\bar{X}$ = 116	$\bar{X}$ = 76	$\bar{X}$ = 101
	σ = 8	σ = 13	σ = 19	σ = 23	σ = 6
	CV = 7.7%	CV = 12.2%	CV = 16.1%	CV = 33%	CV = 5.8%
1C/4 days	96	106	92	30	114
2C	96	107	99	69	93
3C	108	124	111	85	99
3C	105	124	115	88	99
	$\bar{X}$ = 101	$\bar{X}$ = 115	$\bar{X}$ = 104	$\bar{X}$ = 68	$\bar{X}$ = 101
	σ = 6	σ = 10	σ = 11	σ = 27	σ = 9
	CV = 6.1%	CV = 8.7%	CV = 10.2%	CV = 39.2%	CV = 8.8%

*ppm - Calculated from a standard curve. (Concentration vs. Peak Area.)
Mean = $\bar{X}$
Standard Deviation = σ
Coefficient of Variation = $\sigma/\bar{X}$ = CV

TABLE 7 (Cont'd)

Gas Sampling and Storage Study Analytical Data

Sample Container: Ace Thred Glass Bulbs (C)

COMPOUND CONCENTRATION, ppm* (v/v)

Sample / Time	Ethane	Propylene	Methyl Chloride	Methanol	Ethylene Oxide
1C/7 days	83	96	94	72	115
2C	100	92	94	88	93
3C	109	109	121	108	105
4C	109	112	121	112	96
	$\bar{X}$ = 100	$\bar{X}$ = 102	$\bar{X}$ = 108	$\bar{X}$ = 95	$\bar{X}$ = 102
	σ = 12	σ = 16	σ = 16	σ = 19	σ = 10
	CV = 12.2%	CV = 9.5%	CV = 14.5%	CV = 19.5%	CV = 9.6%
1C/14 days	95	105	100	116	87
2C	105	109	105	106	94
3C	100	136	120	61	81
4C	138	134	125	116	93
	$\bar{X}$ = 110	$\bar{X}$ = 121	$\bar{X}$ = 113	$\bar{X}$ = 100	$\bar{X}$ = 89
	σ = 19	σ = 16.3	σ = 11.9	σ = 26.2	σ = 6.0
	CV = 17.3%	CV = 13.4%	CV = 10.6%	CV = 26.3%	CV = 6.8%

* ppm = Calculated from standard curve. (Concentration vs. Peak Area)

Mean = $\bar{X}$

Standard Deviation = σ

Coefficient of Variation = $\sigma/\bar{X}$ = CV

Benzene was quantified in duplicate Ace Thred glass sampling bulbs. The calculated mean concentration at 15 days was 143 ppm. This is probably not significantly higher than the original 100 ppm spike since the analytical results for the other five model compounds were also greater than 100 ppm. Benzene therefore appears to be stable in the glass bulbs, within the precision of the measurement.

D. Comparison of Analytical Data for the Three Types of Containers

The data collected for the three containers is summarized in Table 8. Figures 2 to 6 compare the individual compound concentration values for the three types of containers.

Ethane (Figure 2), propylene (Figure 3), and methyl chloride (Figure 4) were apparently stable in all three containers. Benzene was also apparently stable, however the data has not been plotted, because there were too few data points. Substantial methanol (Figure 5) losses were apparent in the two types of polymeric bags. The glass bulb samples did not show similar losses. In the glass containers the methanol concentration showed apparent increases which may not be significant compared to the precision of the measurement. If real, the increases may be due to imperfect mixing in the glass bulb sampled. Ethylene oxide (Figure 6) was apparently stable in the glass bulbs. Ethylene oxide in the polymeric bags did not appear to be as stable, and high coefficients of variation were observed.

E. Nitrogen Blanks in the 5-Layered and Tedlar Bags

The contents of 5-layered and Tedlar bags filled with nitrogen only were analyzed over a period of 14 days. Both containers had interfering gas chromatography peaks in the -161°C to 72°C boiling point range, on the Porapak Q GC column. The heights

Table 3

Summary of Analytical Data

Mean Concentration Data, ppm

	Ethane (a)				Propylene (b)				Methyl Chloride (c)				Methanol (d)				Ethylene Oxide (e)	
	A	A'	B	C	A	A'	B	C	A	A'	B	C	A	A'	B	C	B	C
0	109	114	97	101	114	112	97	102	103	103	96	101	98	91	72	72	61	99
1	107	108	94	104	108	103	99	107	102	97	91	116	52	39	51	76	55	101
3	107		104		108		101		101		103		14		59		41	
4				101				115				104				68		101
7			104	100		100	100	102			104	108			38	95	62	102
8		98				99				91				40				
14	114	96	112	110	108	98	118	121	109	95	93	113	34	51	0	100	44	89

A- 5-Layered Bags
A'- Duplicate - 5-Layered Bags
B - Tedlar Bags
C - Glass Bulbs

(a) Coefficient of variation averaged 6.1%
(b) Coefficient of variation averaged 5.1%
(c) Coefficient of variation averaged 8.5%
(d) Coefficient of variation averaged 20%
(e) Coefficient of variation averaged 17%

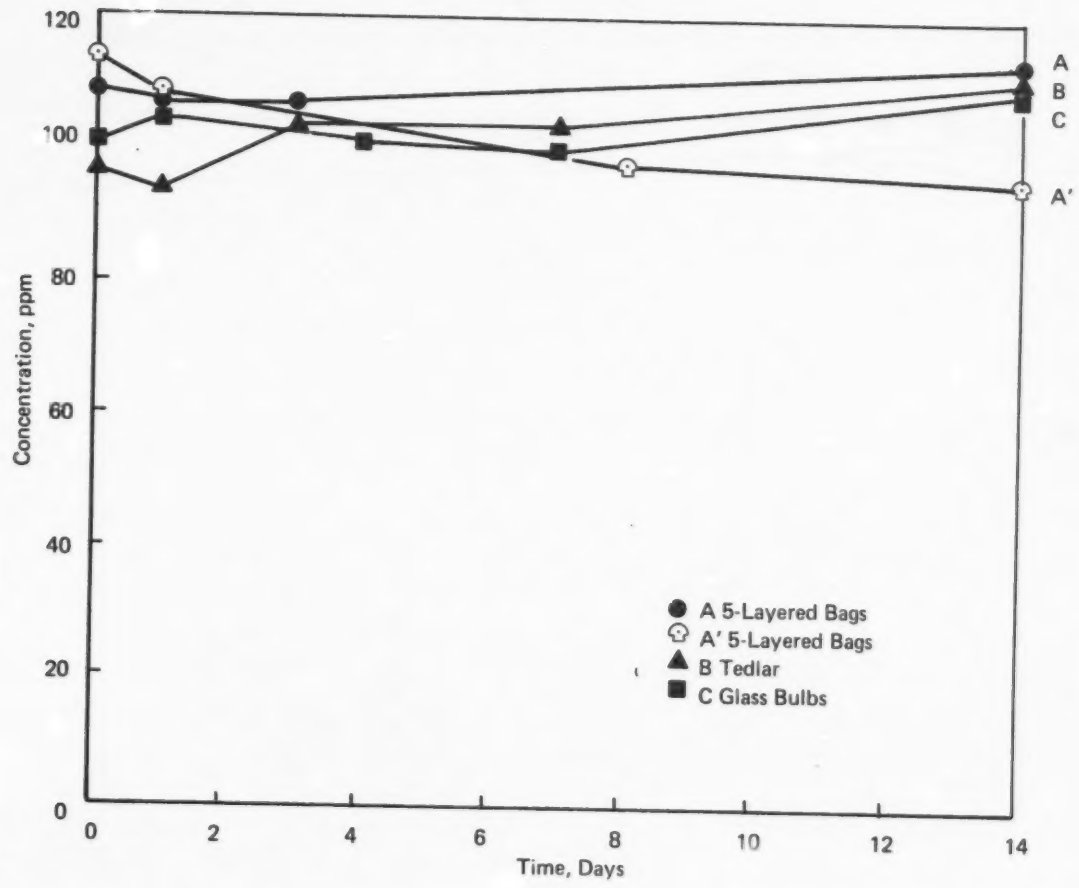

FIGURE 2 ETHANE SAMPLE STABILITY

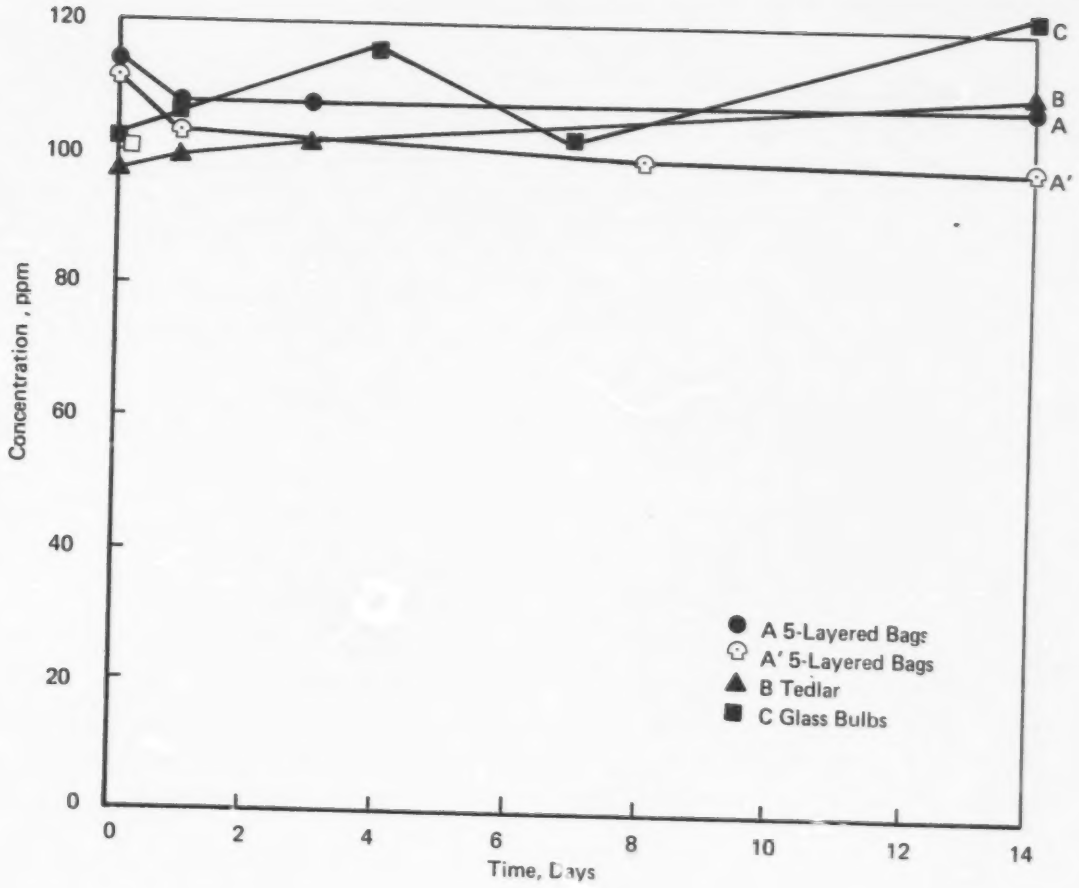

FIGURE 3 PROPYLENE SAMPLE STABILITY

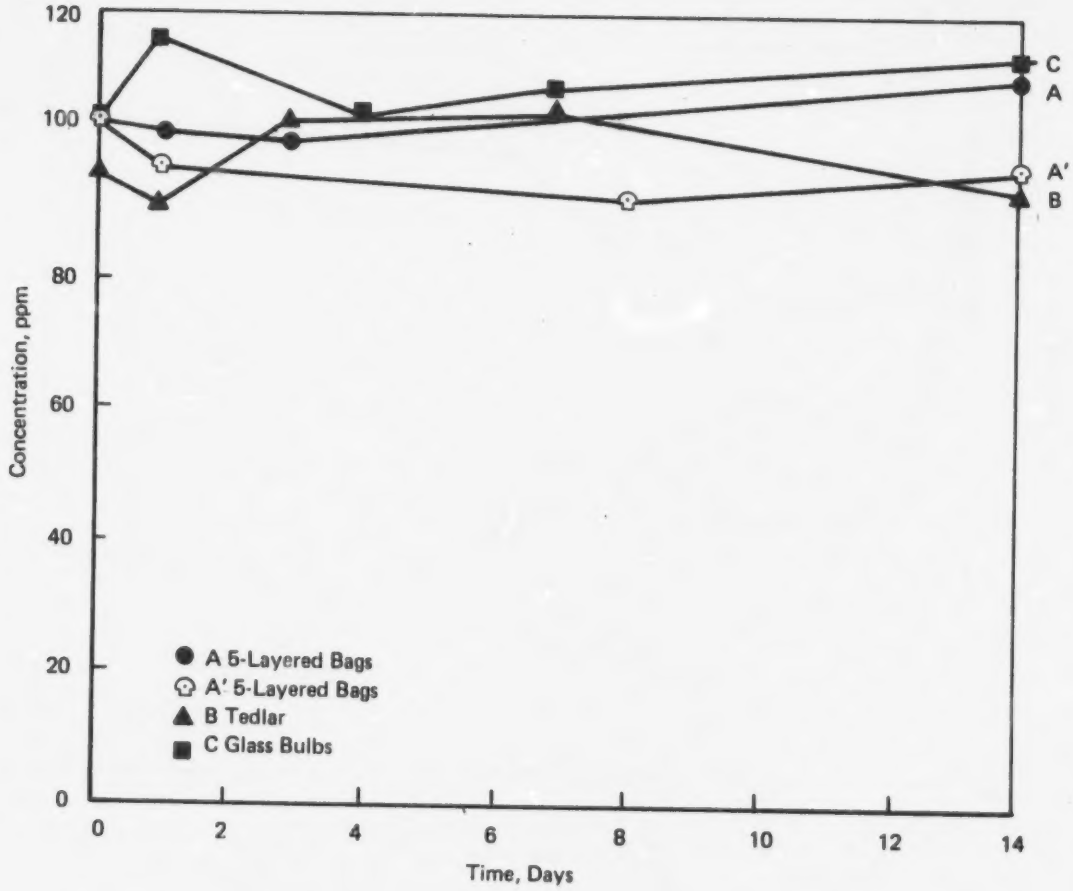

FIGURE 4 METHYL CHLORIDE SAMPLE STABILITY

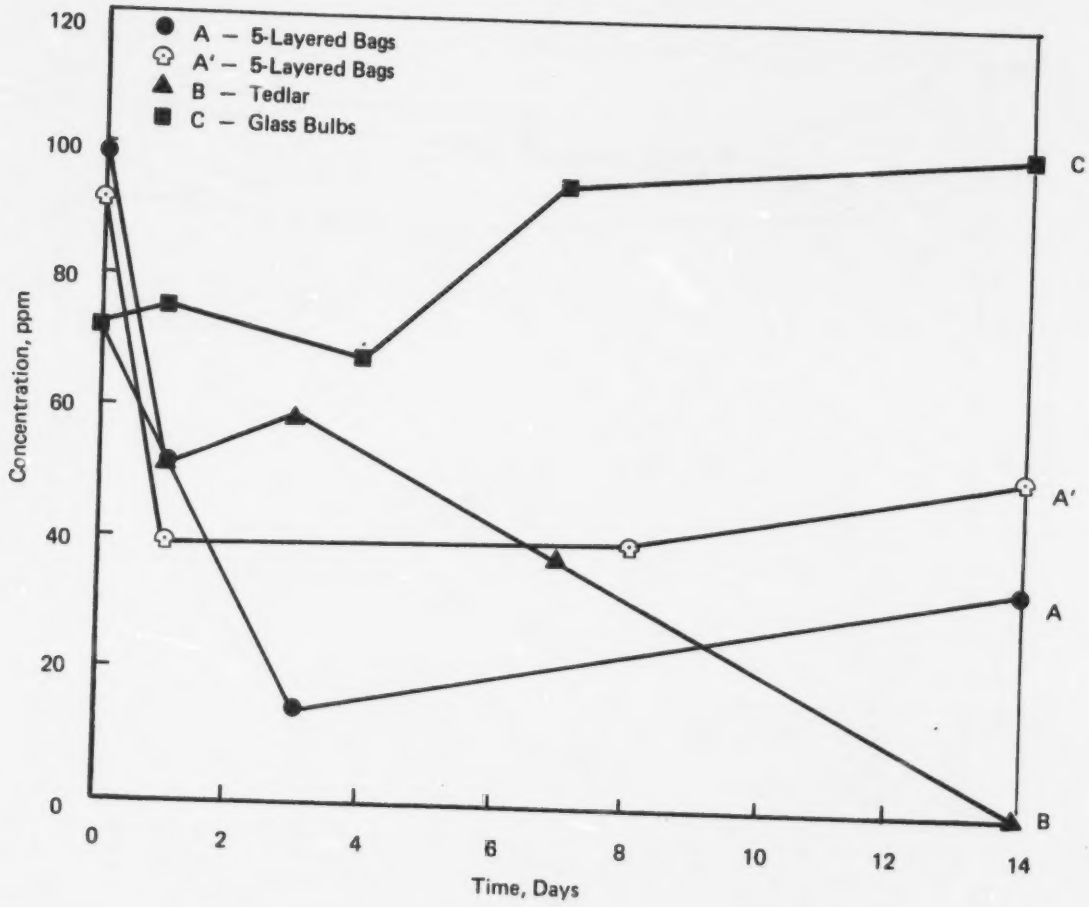

FIGURE 5 METHANOL SAMPLE STABILITY

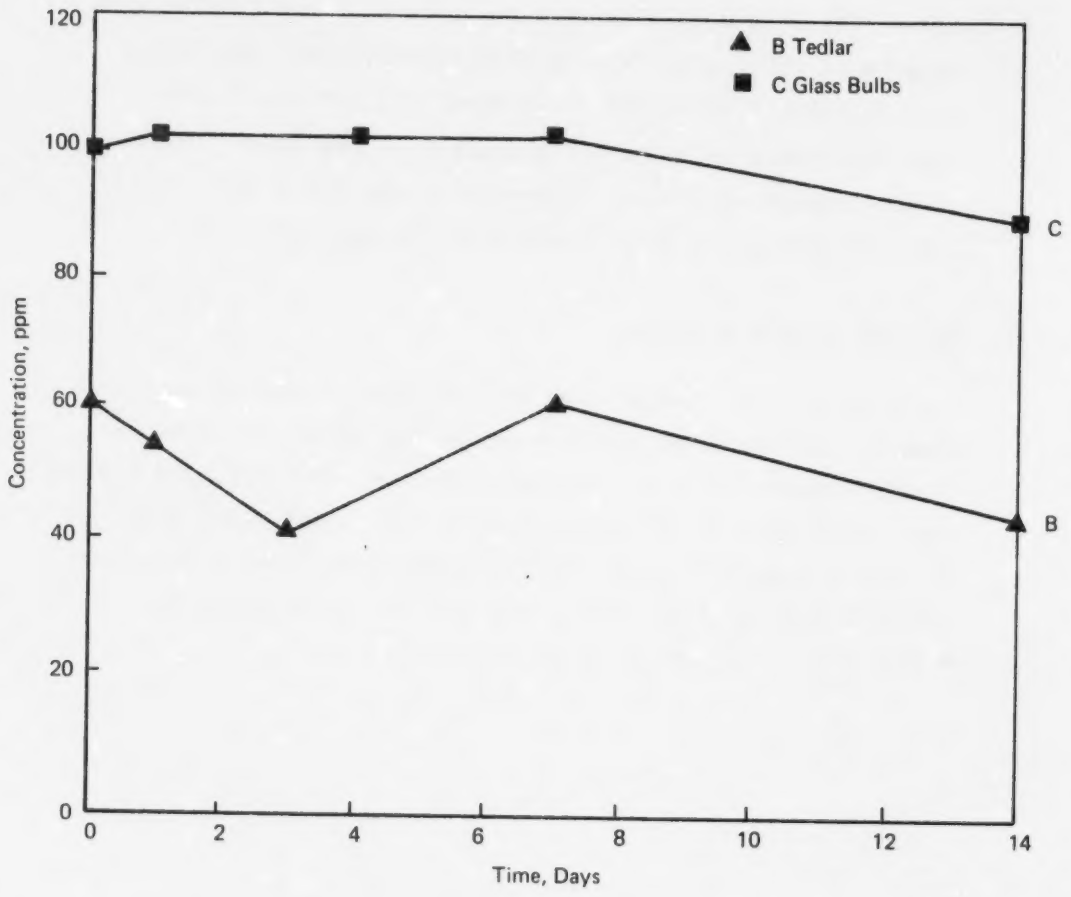

FIGURE 6 ETHYLENE OXIDE SAMPLE STABILITY

of the gas chromatography peaks were compared at 1 day and 7 days. The 5-layered bags show no apparent trend towards loss or gain of those peaks within that time period. The Tedlar bags did show a substantial increase at 1 day and 7 days. These interferences were not a problem in the study presented in this report, which was conducted at the ppm level. The interferences would be of concern at the ppb level.

F. Methanol Preconditioning

The 5-layered and Tedlar bags were checked to see if preconditioning with methanol would decrease the losses in methanol concentration (Table 9). No benefits were observed, and losses were still substantial after storing for 3 days and 7 days. The overall loss was 50%. This finding offers some preliminary evidence that methanol losses may not be due entirely to absorption on the walls of the polymeric bags.

TABLE 9

Gas Sampling Study Analytical Data

Methanol Concentration, ppm (v/v)

Sample / Time	5-Layered Bags		Tedlar Bags	
	1A	2A	1B	2B
0 hr.	147	128	116	105
1.5 hr.	124			
4 hr.	101	101		
3 days	70	74	63	59
7 days	59		32	

VI. CONCLUSIONS AND RECOMMENDATIONS

Overall, glass sampling bulbs were found to be the most satisfactory containers for storing the test gas mixture, as compared to the Tedlar and 5-layered bags.

Calibrated Instruments' 5-layered bags were satisfactory for ethane, propylene, methyl chloride, ethylene oxide and benzene. Methanol, however, did not show adequate storage stability. The experiments run to check whether preconditioning the 5-layered bags with methanol would decrease methanol losses, did not indicate that this technique would be successful. Some interfering gas chromatography peaks were observed from the 5-layered bags, which would interfere at ppb analysis in the -161°C to 72°C boiling point range.

Single-layer Tedlar bags were also satisfactory for ethane, propylene, methyl chloride and benzene in terms of storage stability. However, substantial interfering gas chromatography peaks which increased with time were observed in samples taken from the Tedlar bags. The interferences have been observed and studied by other investigators[9,10], who have concluded that these GC peaks are contaminants in the polymeric bags, presumably the result of outgassing from the materials used to construct the bag. In this study, the interferences were observed in the -160°C to 72°C boiling point range, and as observed for the 5-layered bags, would be of concern at ppb concentration levels. Ethylene oxide results were erratic and methanol was not stable. As in the 5-layered bags, methanol preconditioning of Tedlar bags did not decrease methanol losses. Furthermore, the Tedlar bags were fragile and prone to develop leaks.

Glass sampling bulbs showed no significant deterioration in stored samples. Coefficients of variation for analyses of replicate samples were somewhat higher than expected, perhaps reflecting difficulties in mixing the samples within the bulbs. Mixing difficulties could possibly be minimized by using glass beads. The glass sampling bulbs can be cleaned and silanized, decreasing the potential memory problems from reusing containers. There are doubts as to whether or not the polymeric bags could be cleaned sufficiently to eliminate "memory effects" from previous gas sampling. The polymeric bags would appear

to be more convenient for field sampling and shipping. However, the cylindrical glass sampling bulbs used in this study do seem to be quite rugged. High vacuum stopcocks can be used with the glass bulbs to prevent leakage around the sampling valves during sample shipment.

The study indicates that glass sampling bulbs are the best overall choice, in terms of gas storage stability, and are recommended for collecting relatively small volumes of gas samples. Most compounds in the low boiling point range, with the exception of certain reactive species, may be readily and reliably identified and quantitatified by gas chromatography/mass spectroscopy (GC/MS) analysis methods. In terms of the analysis method detection limits, it will be sufficient for Level 1 on-site gas analysis and GC/MS analysis purposes, in most cases, to collect the equivalent of 0.1 to 3.0 liters of gas sample as grab or time integrated samples. These quantities are conveniently collected in glass sample bulbs.

However, if much larger volumes are required, e.g., 500 liters for biotesting, the polymeric bags are almost certainly more appropriate. This study indicates that the 5-layered bag is superior to the Tedlar bag, and would be appropriate for sampling non-polar gases at ppm levels. When collecting very large samples, the increased container size has been suggested[6,10] as a means of decreasing sample losses by minimizing the container walls' absorptive affects, minimizing water condensation and slowing down reactions among sample components.

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